

Form PTO-1390

U.S. DEPARTMENT OF COMMERCE  
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

P21009

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371U.S. APPLICATION NO. (If known, see 37 CFR  
1.5)

09/856474

INTERNATIONAL APPLICATION NO.

PCT/EP99/09465

INTERNATIONAL FILING DATE

3 December 1999

PRIORITY DATE CLAIMED

10 December 1998

TITLE OF INVENTION  
HARDENABLE MATERIALS WHICH CONTAIN URETDIONE GROUPS, METHOD FOR THE PRODUCTION AND PROCESSING THEREOF,  
AND THEIR UTILIZATION

APPLICANT(S) FOR DO/EO/US

Frank LEHMANN, Michaela GEDAN-SMOLKA, and Dieter LEHMANN

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371 (c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).  
"Unexecuted"
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (U.S.C. 371(c)(5)).

Items 11 to 16 below concern other document(s) or information included:

11. Assignee: INSTITUT FÜR POLYMERFORSCHUNG DRESDEN E.V. of Dresden, GERMANY
12. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
13. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
14. ☐ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ Figure of Drawing to be published \_\_\_\_\_
18. ☒ Other items or information:  
Cover Sheet and International Application as published in German.  
PCT/RO/101-PCT Request(in German).  
PCT/IPEA/409-with five sheets of amended pages(in German).  
PCT/IPEA/416(in German).  
PCT/IB/301.  
PCT/IB/304.  
PCT/IB/308.  
PCT/IB/332.  
PCT/ISA/220(in German).  
PCT/ISA/210(in German).  
Cover Letter under 35 USC 371 and 1.495.  
Claim of Priority.

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
09/856474		PCT/EP99/09465		P21009	
19. <input checked="" type="checkbox"/> The following fees are submitted:  Basic National Fee (37 CFR 1.492(a)(1)-(5)):  Search report has been prepared by the EPO or JPO. . . . . \$ 860.00  International preliminary examination fee paid to USPTO (37 CFR 1.482). . . . . \$ 690.00  No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO(37 CFR 1.445(a)(2)). . . . . \$ 710.00  Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO. . . . . \$1,000.00  International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). . . . . \$ 100.00  ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS	PTO USE ONLY
Surcharge of \$130.00 for furnishing the oath or declaration later than ___ 20 ___ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
Claims	Number Filed	Number Extra	RATE		
Total Claims	- 20 =		X \$18.00	\$	
Independent Claims	- 3 =		X \$80.00	\$	
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$860.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	
SUBTOTAL =				\$860.00	
Processing fee of \$130.00 for furnishing the English translation later than ___ 20 ___ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+	
Extension of Time fee in the amount of \$					
TOTAL NATIONAL FEE =				\$860.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+	
TOTAL FEES ENCLOSED =				\$860.00	
				Amount to be refunded	\$
				Charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$860.00 to cover the above fees is enclosed.					
b. ___ Please charge my Deposit Account No. ___ in the amount of \$ ___ to cover the above fees.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-0089.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.187(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO CUSTOMER NO. 7055 AT THE PRESENT ADDRESS OF: Neil F. Greenblum GREENBLUM & BERNSTEIN, P.L.C. 1941 Roland Clarke Place Reston, VA 20191 (703) 716-1191					
				SIGNATURE Neil F. Greenblum NAME	33084
				28,394 REGISTRATION NUMBER	

09/856474

P21009.A01

Rec'd PCT/EP 31 JUL 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : F. LEHMANN et al.

Appl. No : 09/856,474  
(U.S. National Phase of PCT/EP99/09465)

I.A. Filed: December 3, 1999

For : HARDENABLE MATERIALS WHICH CONTAIN URETDIONE GROUPS,  
METHOD FOR THE PRODUCTION AND PROCESSING THEREOF,  
AND THEIR UTILIZATION

**PRELIMINARY AMENDMENT AND COVER LETTER  
SUBMITTING AMENDED PAGES OF APPLICATION**

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

Sir:

Applicants submit herewith another copy of the International Preliminary Examination Report and its Annex, which was previously submitted when entering the national stage on June 8, 2001, accompanied by an English Translation of the Annex.

In particular, Applicants submit herewith an English translation including replacement sheets 12-16 containing claims 1-23 which are an English translation of replacement pages of claims 1-5 included as an Annex to the International Preliminary Examination Report.

Applicants respectfully point out that replacement pages 12-16 contain claims 1-23 upon which the International Preliminary Examination Report is based, and replaces claims 1-24 of the originally filed application.

Based on the above, Applicants respectfully request examination on the merits of the literal English application containing substitute pages 12-16.

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Additionally, prior to the examination of the above-identified modified application, entry of the following amendment of replacement pages 12-16 is request, so as to remove multiple dependent claims and to add the second claim 13 as new claim 24.

IN THE CLAIMS

Please amend the claims as follows (a marked-up copy of the claim amendments is provided as an attachment to this Amendment):

9. (Amended) Masses according to claim 1, in which the component (C) comprises any desired mixtures of at least one metalorganic catalyst of:

(a) the general formula



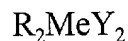
in which

Me means metal,

R means alkyl residue, and

X means carboxyl residue; and

(b) the general formula



in which

Me means metal,

R means alkyl residue, and

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Y means alcoholate residue; and

(c) the general formula



in which

Me means metal,

Z means acetylacetonate residue, and

n means 2 or 3; and derivatives thereof; and

at least one derivative of the metalorganic compounds.

12. (Amended) Process for the production of hardenable masses containing uretdione groups according to claim 1, in which masses containing uretdione groups that are not cross-linked are used as original material, which consist of (A) a linear or branched bonding agent component having terminal and/or side chain hydroxyl groups with a hydroxyl number of 25 to 400 and an average molecular weight of 400 to 20,000, which is present in a fluid or viscous form above the reaction or processing temperature, with (A1) either the bonding agent component being free of carboxyl groups or (A2) the concentration of carboxyl groups being less than the concentration of the active catalyst (C) or (A3), in the case of a higher concentration of carboxyl groups in relation to the catalyst concentration (C) used, such an amount of reactive agent is added that is necessary to block the amount of carboxyl groups in order to realize a required

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concentration of the active catalyst (C), and (B) a polyaddition compound present in a fluid or viscous form above the reaction or processing temperature and containing uretdione groups and, optionally, free isocyanate groups and based on aliphatic and/or cycloaliphatic diisocyanates, and (C) at least one active or reactively activatable Lewis acid catalyst, and (D) other catalysts known from urethane chemistry and (E) auxiliary materials and additives that are known per se, where D) and E) can be added, these original materials are homogenized in solution and/or in melt at the longest until an increase in molar mass can be verified, then the solution or melt is quickly cooled to below the reaction temperature of the mass and subsequently the hardenable mass can be stored and then or subsequently to cooling the further processing of the hardenable mass to complete cross-linking is performed, with the temperature being linearly and/or non-linearly increased and/or kept constant at the reaction temperature sufficiently long until essentially no more reaction heat can be verified by means of DSC measurements.

23. (Amended) Use of the masses according to claim 1 for coating heat-resistant and thermolabile substrates, for masking components, as a treatable, hardenable coating form and as a thermally hardenable molding compound and a thermally hardenable surfacer.

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Please cancel the second claim 13 without prejudice or disclaimer of the subject matter recited therein.

Please add claim 24, as follows:

24. Process according to claim 12, in which the homogenization of the hardenable masses occurs at temperatures less than or equal to 110°C, preferably between 50 and 100°C.

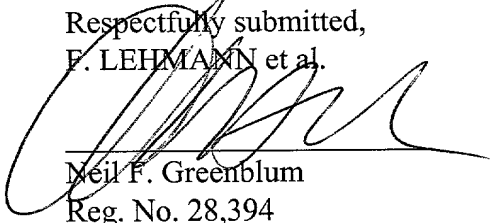
REMARKS

Entry of the foregoing amendment, upon which the International Preliminary Examination Report is based, prior to examination and calculation of the filing fees to remove multiple dependent claims and to add the second claim 13 as new claim 24 in the above-identified patent application is respectfully requested.

Should there be any questions, the Examiner is invited to contact the undersigned at the below listed number.

July 30, 2001  
Greenblum & Bernstein, P.L.C.  
1941 Roland Clarke Place  
Reston, VA 20191  
(703) 716-1191

Respectfully submitted,  
F. LEHMANN et al.

  
Neil F. Greenblum  
Reg. No. 28,394

*Reg. No. 33,094*

MARKED-UP COPY OF AMENDED CLAIMS

9. (Amended) Masses according to claim 1, in which the component (C) comprises any desired mixtures of [the above-mentioned metalorganic catalysts and derivatives according to claims 5 to 8]at least one metalorganic catalyst of:

(a) the general formula



in which

Me means metal,

R means alkyl residue, and

X means carboxyl residue; and

(b) the general formula



in which

Me means metal,

R means alkyl residue, and

Y means alcoholate residue; and

(c) the general formula



in which



Me means metal,

Z means acetylacetonate residue, and

n means 2 or 3; and derivatives thereof; and

at least one derivative of the metalorganic compounds.

12. (Amended) Process for the production of hardenable masses containing uretdione groups according to [at least one of claims 1 to 11] claim 1, in which masses containing uretdione groups that are not cross-linked are used as original material, which consist of (A) a linear or branched bonding agent component having terminal and/or side chain hydroxyl groups with a hydroxyl number of 25 to 400 and an average molecular weight of 400 to 20,000, which is present in a fluid or viscous form above the reaction or processing temperature, with (A1) either the bonding agent component being free of carboxyl groups or (A2) the concentration of carboxyl groups being less than the concentration of the active catalyst (C) or (A3), in the case of a higher concentration of carboxyl groups in relation to the catalyst concentration (C) used, such an amount of reactive agent is added that is necessary to block the amount of carboxyl groups in order to realize a required concentration of the active catalyst (C), and (B) a polyaddition compound present in a fluid or viscous form above the reaction or processing temperature and containing uretdione groups and, optionally, free isocyanate groups and based on aliphatic and/or cycloaliphatic diisocyanates, and (C) at least one active or reactively activatable Lewis acid catalyst, and (D) other catalysts known from urethane chemistry and (E) auxiliary materials and additives that are known per se, where D) and E) can be added, these original materials are homogenized in solution and/or in melt at the longest until an increase in molar mass can be

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verified, then the solution or melt is quickly cooled to below the reaction temperature of the mass and subsequently the hardenable mass can be stored and then or subsequently to cooling the further processing of the hardenable mass to complete cross-linking is performed, with the temperature being linearly and/or non-linearly increased and/or kept constant at the reaction temperature sufficiently long until essentially no more reaction heat can be verified by means of DSC measurements.

23. (Amended) Use of the masses according to [claims 1 to 8] claim 1 for coating heat-resistant and thermolabile substrates, for masking components, as a treatable, hardenable coating form and as a thermally hardenable molding compound and a thermally hardenable surfacer.

Attachment 1

Modified claims for PCT/EP99/09465

Claims

1. Hardenable masses containing uretdione groups containing (A) a linear or branched bonding agent component having terminal and/or side chain hydroxyl groups with a hydroxyl number of 25 to 400 and an average molecular weight of 400 to 20,000, which is present in a fluid or viscous form above the reaction or processing temperature, with (A1) either the bonding agent component being free of carboxyl groups or (A2) the concentration of carboxyl groups being less than the concentration of the active catalyst (C) or (A3), in the case of a higher concentration of carboxyl groups in relation to the catalyst concentration (C) used, such an amount of reactive agent is added that is necessary to block the amount of carboxyl groups in order to realize a required concentration of the active catalyst (C), and (B) a polyaddition compound present in a fluid or viscous form above the reaction or processing temperature and containing uretdione groups and, optionally, free isocyanate groups and based on aliphatic and/or cycloaliphatic diisocyanates, and (C) at least one active or reactively activatable Lewis acid catalyst,

**where (C1), in the case of (A1) and (A2), the use of Lewis acid carboxylates as catalysts is excluded and with (C2), in the case of (A3), Lewis acid carboxylates also being included that are or may be reactivated by means of alkylating agents to carbonic acid esters and while forming Lewis acid alcoholates**

and (D) other catalysts known from urethane chemistry and (E) auxiliary materials and additives that are known per se, where D) and E) can be added.

2. Masses according to claim 1, in which the component A) comprises

a polymer compound having hydroxyl groups such as, for example, polyacrylates, polyethers, polyesters, and oligo- and/or polyepoxides.

3. Masses according to claim 1, in which the component B) comprises a polyaddition compound based on isophorone diisocyanate and/or hexamethylene diisocyanate having uretdione groups and optionally free isocyanate groups.

4. Masses according to claim 1, in which the reactive agent is an epoxy compound and/or an oxazoline compound.

5. Masses according to claim 1, in which the component C) comprises at least one metalorganic catalyst of the general formula



in which

Me means metal,

R means alkyl residue, and

X means carboxyl residue.

6. Masses according to claim 1, in which the component C) comprises at least one metalorganic catalyst of the general formula



in which

Me means metal,

R means alkyl residue, and

Y means alcoholate residue.

7. Hardenable masses according to claim 1, characterized in that the component C) comprises at least one metalorganic catalyst of the general formula



in which

Me means metal,

Z means acetylacetonate residue, and

n means 2 or 3.

8. Masses according to claim 1, in which the component C) comprises at least one derivative of the metalorganic catalyst according to claims 5 to 7.

9. Masses according to claim 1, in which the component (C) comprises any desired mixtures of the above-mentioned metalorganic catalysts and derivatives according to claims 5 to 8.

10. Masses according to claim 1, in which the component D) comprises nucleophilic substances.

11. Masses according to claim 1, in which the component A) has a hydroxyl number of 25 to 200 and an average molecular weight of 1,000 to 10,000.

12. Process for the production of hardenable masses containing uretdione groups according to at least one of claims 1 to 11, in which masses containing uretdione groups that are not cross-linked are used as original material, which consist of (A) a linear or branched bonding agent component having terminal and/or side chain hydroxyl groups with a hydroxyl number of 25 to 400 and an average molecular weight of 400 to 20,000, which is present in a fluid or viscous form above the reaction or processing temperature, with (A1) either the bonding agent component being free of carboxyl groups or (A2) the concentration of carboxyl groups being less than the concentration of the active catalyst (C) or (A3), in the case of a higher concentration of carboxyl groups in relation to the catalyst concentration (C) used, such an amount of reactive agent is added that is necessary to block the amount of carboxyl groups in order to realize a required concentration of the active catalyst (C), and (B) a polyaddition compound present in a fluid or viscous form above the reaction or processing temperature and containing uretdione groups and, optionally, free isocyanate groups and based on aliphatic and/or cycloaliphatic diisocyanates, and (C) at least one active or reactively activatable Lewis acid catalyst, and (D) other catalysts known from urethane chemistry and (E) auxiliary materials and additives that are known per se,

where D) and E) can be added, these original materials are homogenized in solution and/or in melt at the longest until an increase in molar mass can be verified, then the solution or melt is quickly cooled to below the reaction temperature of the mass and subsequently the hardenable mass can be stored and then or subsequently to cooling the further processing of the hardenable mass to complete cross-linking is performed, with the temperature being linearly and/or non-linearly increased and/or kept constant at the reaction temperature sufficiently long until essentially no more reaction heat can be verified by means of DSC measurements.

13. Process according to claim 12 in which the homogenization of the hardenable masses in the melt takes place in a laboratory kneader or in a co-kneader and/or an extruder.

13. Process according to claim 12, in which the homogenization of the hardenable masses occurs at temperatures less than or equal to 110°C, preferably between 50 and 100°C.

14. Process according to claim 12, in which the homogenization of the hardenable mass is performed for up to 30 min.

15. Process according to claim 12, in which the cooling below the reaction temperature occurs after the homogenization of the hardenable masses by insertion of the melt into liquid nitrogen or by applying it to a cooling belt.

16. Process according to claim 12, in which at least one of the components (A) to (E), preferably (A) and (B), is used in a fluid form.

17. Process according to claim 12, in which the temperature is increased linearly and/or non-linearly in a range of preferably 20 K above the homogenization temperature up to a maximum of 190°C, preferably up to 160°C.

18. Process according to claim 12, in which the addition of the catalyst or catalyst mixture as a batch is performed after the homogenization of the components A, B, C, and E at reduced temperatures.

19. Process according to claim 12, in which the homogenization of the hardenable masses occurs in a melt.

20. Process according to claim 12, in which the homogenization of the hardenable masses is performed in one or more stages in a melt, with the catalyst being added at lower temperatures in the case of single-stage homogenization and, in the case of multi-stage homogenization, is not added until the second stage at lower temperatures.

21. Process according to claim 12, in which the temperature is increased in stages and the temperature is kept constant after every increasing step for a time period of 1 to 60 minutes, more advantageously 5 to 30 minutes.

22. Process according to claim 12, in which the temperature is increased in two stages, with the second increase in temperature being performed immediately thereafter or temporally later.

23. Use of the masses according to claims 1 to 8 for coating heat-resistant and thermolabile substrates, for masking components, as a treatable, hardenable coating form and as a thermally hardenable molding compound and a thermally hardenable surfacer.

09/856474

Rec'd PCT/PTO 31 JUL 2001

VERIFICATION OF TRANSLATION

I, AMY JACOBSON

of 1941 Roland Clarke Place  
Reston, VA 20191

declare that I am well acquainted with both the German and English languages, and that the attached is a literal translation, to the best of my knowledge and ability, of the German language Patent Application No. PCT/EP99/09465, filed December 3, 1999.

Signature Amy Jacobson  
AMY JACOBSON

Date July 26, 2001



# HARDENABLE MASSES CONTAINING URETDIONE GROUPS AND A PROCESS FOR THEIR PRODUCTION AND PROCESSING AS WELL AS THEIR USE

**[0001]** The invention relates to the field of chemistry and concerns hardenable masses, such as are used, for example, for the production of coatings, and a process for their production and processing.

**[0002]** The blocking of isocyanates by means of dimerization to uretdiones is an effective method of protecting isocyanate groups from premature reaction. The coating of heat-resistant substrates, in particular with powder coatings, is an important area of application for hardeners containing uretdione groups.

**[0003]** Powder coatings are free of solvents and, as a result, are free of harmful emissions to a large extent and they have a very high coating equivalent. Thus, powder coating is a very environmentally friendly and economical coating method.

**[0004]** Polyurethane-based coatings especially distinguish themselves with special light and weather resistance and excellent optical characteristics. The polyurethane powder coatings used today in practice are based on polyesters carrying fixed hydroxyl groups as well as fixed aliphatic and/or cycloaliphatic polyisocyanates whose isocyanate functions are protected by external, low-molecular masking agents. These masking agents escape at least partially during the thermal hardening of the powder coating. These emissions run contrary to the principle of a lack of emissions in powder coating formulations and, for reasons of ecology and workplace hygiene, require special provisions.

**[0005]** By using cross linkers containing uretdione groups (e.g., DE 23 12 391 OS, EP 045 998 A1, EP 669 353 A1), the possibility exists of avoiding such emissions of low-molecular substances. Due to the low level of reactivity of the internally blocked isocyanate groups, the use of corresponding hardeners containing uretdione groups has been limited up to the present day because the

temperatures necessary for hardening greater than 160°C are too high and/or the time necessary for hardening is too long. In view of the costs of energy and the possibility of coating thermolabile substrates (e.g., plastic or wood), it is necessary to increase the reactivity of such systems.

**[0006]** Various attempts have been made to accelerate the hardening of polyurethane masses based on hardeners containing uretdione groups by using catalysts. A series of compounds has been suggested, such as the known metalorganic catalysts known from polyurethane chemistry such as tin (II) acetate, tin (II) octoate, tin (II) ethyl caproate, tin (II) laurate, dibutyltin diacetate, dibutyltin dilaureate, dibutyltin maleate (e.g., EP 045 994 A1, EP 045 998 A1, WO 91/07452, or DE 24 20 475), iron (III) chloride, zinc chloride, zinc 2 ethyl caproate, and molybdenum glykolate or tertiary amines such as triethylamine, pyridine, methylpyridine, benzyl dimethylamine, N,N endo ethylenepiperazine, N methylpiperidine, pentamethyldiethylene triamine, N,N dimethylaminocyclohexane, and N,N' dimethylpiperazine (e.g.,n EP 639 598 A1).

**[0007]** Generally, organic tin compounds of the type mentioned are used in practice. The increases in reactivity that can be achieved by means of these catalysts do not yet meet the requirements of masses hardening at low temperatures.

**[0008]** In EP 803 524 A1, compounds containing N,N' trisubstituted amidines as breakdown catalysts are described. The object of this prior art is a polyurethane powder coating that contains a bonding agent component having hydroxyl groups, a polyaddition compound having uretdione groups and, optionally, free isocyanate groups based on aliphatic and/or cycloaliphatic diisocyanates, at least one N,N,N' trisubstituted catalyst containing amidine structures with an amidine group content (calculated as CN<sub>2</sub>; molecular weight = 40) of 12.0 to 47.0 wt-%, optionally other catalysts known from polyurethane chemistry, and optionally other auxiliary agents and additives known from powder coating technology. The bonding agent components having hydroxyl groups are

added to the powder coating in such amounts that 0.6 to 1.4, preferably 0.8 to 1.2 isocyanate groups of the uretdione groups and optionally polyaddition compounds having free isocyanate groups occur on each hydroxyl group of the bonding agent component, with isocyanate groups being understood as the total of isocyanate groups present in dimeric form and free isocyanate groups. In the publication, possible hardening temperatures of 130°C and up are mentioned. However, it can be seen in the exemplary embodiments that, at hardening temperatures up to 170°C, coatings of a high degree of quality are not achieved.

**[0009]** The object of the present invention is to provide masses containing uretdione groups with a high reactivity that harden at lower temperatures in the same amount of time or at the same temperature in a considerably shorter amount of time than the masses containing uretdione groups known up to now.

**[0010]** The object is attained by means of the invention in accordance with claims 1 and 11. Further developments are the object of the subclaims.

**[0011]** It was possible to attain this object by providing the masses according to the invention. The masses according to the invention are based on the fact that, under the conditions according to the invention, Lewis acid catalysts, in particular metalorganic compounds, accelerate the transformation of uretdione groups with hydroxyl groups so strongly that, with their help and using the known uretdione hardeners, masses can be produced that already harden at comparatively low temperatures in the same amount of time or at the same temperatures in a considerably shorter period of time than the masses containing uretdione hardeners that have been known up to now.

**[0012]** The invention relates to masses containing uretdione groups that are hardenable at low temperatures containing A) a bonding agent component having hydroxyl groups, B) a polyaddition compound having uretdione groups and optionally free isocyanate groups as a cross-linker, C) at least one active or reactively activatable Lewis acid catalyst, optionally D) further catalysts known from polyurethane chemistry, and optionally E) auxiliary agents and additives that

are known per se, provided that (A1) the bonding agent component is free of carboxyl groups or (A2) the concentration of carboxyl groups is less than the concentration of active catalyst (C) or (A3) in the case of a higher concentration of carboxyl groups with regard to the concentration of the catalyst (C) used such an amount of reactive agent such as, for example, epoxy compound or oxazoline is added that is necessary for blocking the amount of carboxyl groups for achieving the required concentration of the active catalyst (C).

**[0013]** The object of the invention is also the use of the masses for coating of heat-resistant and thermolabile substrates, for masking of components, as a treatable, hardenable molding compound, and as a thermally hardenable surfacer.

**[0014]** The component A) contained in the mass according to the invention is a bonding agent having any unspecified hydroxyl group with a hydroxyl number of 25 to 400, preferably 25 to 200 and an average molecular weight of 400 to 20,000, preferably 1,000 to 10,000, which is present above the reaction or treatment temperature in a liquid or viscous form. Such bonding agents are, for example, polyesters, polyacrylates, polyethers, or polyurethanes containing hydroxyl groups, as well as any unspecified mixtures of such resins.

**[0015]** The component B) contained in the mass according to the invention is a polyaddition compound that is present in a liquid or viscous form above the reaction or treatment temperature that contains uretdion groups and, optionally, free isocyanate groups based on aliphatic and/or cycloaliphatic diisocyanates, in particular those based on 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 4,4'-diisocyanatodicyclohexylmethane, 1,3 diisocyanato-2(4)-methylcyclohexane, or any unspecified mixture of these diisocyanates, with HDI and IPDI being preferred.

**[0016]** The component B) is used in the masses according to the invention in such amounts that, on every hydroxyl group of the bonding agent component A), 0.8 to 2.4, preferably 0.9 to 2.2 isocyanate groups of the component B) occur;

isocyanate groups of component B) is to be understood as the sum of isocyanate groups present in dimeric form as uretdion groups and free isocyanate groups.

**[0017]** In order to accelerate hardening, the masses according to the invention contain Lewis acid catalysts C), preferably metalorganic compounds such as, for example, of the tin and/or zinc and/or cadmium and/or iron and/or manganese and/or molybdenum and/or aluminum and/or cobalt and/or zirconium type in the absence or presence of tertiary amine and/or present or reactively forming ammonium and/or N,N,N' trisubstituted amidine and/or present or reactively forming phosphonium and/or imidazole and/or epoxy compounds for activating or increasing the effects of the catalyst.

**[0018]** Catalysts C) that may be used are metalorganic compounds of the general formula



in which

Me means metal,

R means alkyl residue, and

X means carboxyl residue

as well as metalorganic compounds of the general formula



in which

Me means metal,

R means alkyl residue, and

Y means alcoholate residue

as well as metalorganic compounds of the general formula



in which

Me means metal,

Z means acetylacetonate residue, and

n = 2 or 3,

or any unspecified mixtures of such metalorganic catalysts.

[0019] Catalysts C) that may be used are also derivatives of the above-mentioned compounds from consecutive reactions such as, for example, hydrolysis and decomposition products or any unspecified mixtures of these derivatives or any unspecified mixtures of the above-mentioned catalysts with these derivatives.

[0020] The catalysts C) are used in the masses according to the invention in an amount of 0.01 to 5.0 wt-%, preferably 0.1 to 3.0 wt-%, in relation to the total amount of components A) to D).

[0021] Optionally, compounds known from polyurethane chemistry may also be used in the masses according to the invention as further catalysts D).

[0022] Optionally, masses according to the invention can contain auxiliary materials and additives (E) that are known per se, such as flow improvers, light screening agents, UV absorbers, pigments, or color stabilizers, for example.

[0023] The homogenization of the individual components of the mass occurs by means of mixing the components in melts, preferably in a laboratory kneader, co-kneader, or extruder. The temperature and/or mixing time and/or revolutions per minute are adjusted such that, during homogenization, essentially no branching or polymer formation reactions occur yet. First, for example, a melting of component A occurs in the laboratory kneader. Then the addition of components B and E occurs successively. Finally, the dosage of the catalyst C or catalyst mixture C and D occurs, preferably as a batch. For the homogenization in a co-kneader or in an extruder, for example, all components are thoroughly mixed and subsequently homogenized in the co-kneader or extruder. The homogenization of the components occurs at mass temperatures between 50 and 110°C, preferably between 70 and 100°C and lasts up to 30 min. In order to achieve an optimal intermixing, a dual extrusion in the co-kneader or extruder may be advantageous; here, the component C may optionally also not be added until during the second extrusion step.

[0024] The homogenized mass is subsequently solidified by means of quick

cooling. This occurs by means of applying the melt to a cooling belt or insertion in liquid nitrogen. The solidified mass is broken and crushed or, in the case of powder coatings, subsequently ground into powder using a classifier mill with a particle size of  $< 90 \mu\text{m}$ .

**[0025]** The homogenization of the components can also occur in solution. Here, the homogenization temperature lies above room temperature and essentially does not exceed  $110^{\circ}\text{C}$ . Advantageously, at least one of the components (A-E), preferably A and/or B, is present in a fluid form in which at least one of the other components may be dissolved. The homogenized mass is subsequently cooled to temperatures of at least 20 K below the mixing temperature by means of quenching and can then be stored until it is treated.

**[0026]** Highly reactive, thermally hardenable systems may be produced in which the reactive components including catalysts and, optionally, other additives depending on the application are homogenized, for example, by means of melting extrusion and subsequently crushed and/or pulverized and have a sufficiently high storage stability.

**[0027]** In the further processing of the masses according to the invention for coating, the powder coating formulas produced in this manner can be applied to the substrates to be coated using conventional coating processes such as, for example, electrostatic powder spraying or fluid-bed coating. The hardening of the coatings occurs by means of heating to temperatures of  $110$  to  $200^{\circ}\text{C}$ , preferably to temperatures of  $120$  to  $180^{\circ}\text{C}$  until a complete cross-linking is achieved and no more reaction heat can be detected using DSC measurements. Here, the increase in temperature occurs linearly and/or nonlinearly and/or the temperature is kept constant at the reaction temperature. At higher temperatures that correspond to the hardening temperatures of the prior art, hardening occurs in a significantly shorter time. On the other hand, the hardening can be achieved according to the invention at significantly lower temperatures. The hardening of the hardenable masses can be performed, for example, in two or more subsequent or temporally separated

hardening stages at the same or different hardening temperatures.

[0028] After the partial cross-linking of the hardenable masses or, for example, a layer in the first hardening stage, the hardening optionally occurs after treatment in the second hardening stage. During hardening, for example, a chemical coupling of masses or layers in the border surface of the hardenable masses or coatings is possible.

[0029] The first reaction stage is performed at relatively low temperatures, preferably  $\leq 160^{\circ}\text{C}$ . If the amount of the catalyst (C) used is reduced, the temperature for the first reaction stage must be increased and/or the reaction time must be prolonged. The second reaction stage is performed at least at the same reaction temperatures with a considerably longer reaction time or preferably at higher temperatures than the first reaction stage in a shorter time until complete hardening.

[0030] Any unspecified heat-resistant substrates such as, for example, glass or metals, but also thermolabile substrates such as plastics or wood may be coated according to the invention.

[0031] By using the catalysts according to the invention under the conditions described, the conversion of the hardeners containing uretdione groups with bonding agent components containing hydroxyl groups at comparatively low temperatures is possible.

[0032] If the carboxyl group content of the bonding agent component B) equal to or greater than the content of the catalyst C), it is possible to block a sufficient amount of carboxyl groups by adding, for example, epoxy compounds, such that a catalytically effective concentration of the active catalyst C) occurs.

[0033] While the use of dialkyltin carboxylates as catalysts for the cross-linking of bonding agents containing hydroxyl groups with hardeners containing uretdione groups is known according to the prior art, no catalyst activity of the metalorganic compounds described on the conversion of the uretdione function can be discerned under the conditions described. The hardening temperatures of



the masses containing uretdione groups described in the prior art, which have been decreased in comparison to uncatalyzed masses, can rather be attributed to an acceleration of the conversion of the isocyanate groups with hydroxyl groups that have been thermally recovered from the uretdione rings.

**[0034]** The invention will be described in greater detail below with reference to exemplary embodiments.

**[0035]** Example 1 shows the prior art in the form of an uncatalyzed composition.

**[0036] Examples**

**[0036]** The compounds (A) and (B) are homogenized in a laboratory kneader. The temperature of the kneader chamber is adjusted such that the mass temperature does not substantially exceed 90°C. The compounds (E), (D), and (C) are then added to this mass in succession.

**[0037]** The compositions of the exemplary mixtures are provided in Table 1. The characteristics of the components used are provided in Table 2.

**[0038]** The homogenized masses are cooled quickly by insertion in liquid nitrogen. The quickly cooled masses are crushed in a laboratory mill while being cooled and dried at 30°C in a vacuum. The characterization of the samples occurs by means of differential scanning calorimetry (DSC). The tests occur dynamically in a temperature range of 40 to 260°C at a heating speed of 10 K/min. The results are provided in Table 3.

**[0039] Table 1: Composition of the Exemplary Mixtures\***

Components/Example	1	2	3	4	5	6	7	8
(A) Hydroxyl-terminated polyester	75.7	75.7	75.7	75.7	75.7	75.7	-	75.7
(A1) Hydroxyl-terminated polycaprolacton	-	-	-	-	-	-	76.7	-
(A3) Triglycidyl isocyanurate	2.9	2.9	2.9	2.9	2.9	-	-	-

(B) Polyaddition compound containing uretdione groups	24.3	24.3	24.3	24.3	24.3	24.3	24.3	24.3
(C) Dibutyltin dilaurate	-	1.0	-	-	-	-	-	-
(C) Dibutyltin dibutylate	-	-	1.0	-	-	-	-	-
(C) Zinc acetyl acetate	-	-	-	1.0	1.0	1.0	1.0	3.0
(D) Benzyltrimethylammonium chloride	-	-	-	-	1.0	1.0	-	-
(E) Acronal 4F	-	-	-	-	-	0.6	-	-
(E) White pigment	-	-	-	-	-	0.6	-	-

\* all amounts are in wt-%.

[0039] **Table 2: Characteristics of the Components Used in the Examples**

Component	Hydroxyl number	Carboxyl number	Isocyanate equivalent	T <sub>m</sub> (°C)
Hydroxyl-terminated polyester	30	≤5	-	56
Hydroxyl-terminated polycaprolacton	56	≤0.1	-	40-50
Triglycidyl isocyanurate	-	-	-	98
Polyaddition compound containing uretdione groups	-	-	310	54

**Table 3: Results of the Thermal Tests (dynamic)**

Sample Number	1	2	3	4	5	6	7	8
Beginning of the reaction T <sub>onset</sub> (°C)	184.2	144.0	134.9	131.0	128.2	123.6	122.4	119.1
Reaction maximum T <sub>max</sub> (°C)	211.8	164.6	160.3	145.3	145.2	141.6	139.4	141.8

**Table 4: Results of the Thermal Tests (isothermic)**

Example	1	2	3	4	5
Reaction temperature in °C	150	150	150	130	130
Reaction time (min) until the most complete possible cross-linkage	- *)	17	16	12	12

\*) No appreciable cross-linkage noted.

## Claims

1. Hardenable masses containing uretdione groups containing (A) a linear or branched bonding agent component having terminal and/or side chain hydroxyl groups with a hydroxyl number of 25 to 400 and an average molecular weight of 400 to 20,000, which is present in a fluid or viscous form above the reaction or processing temperature, with (A1) either the bonding agent component being free of carboxyl groups or (A2) the concentration of carboxyl groups being less than the concentration of the active catalyst (C) or (A3), in the case of a higher concentration of carboxyl groups in relation to the catalyst concentration (C) used, such an amount of reactive agent is added that is necessary to block the amount of carboxyl groups in order to realize a required concentration of the active catalyst (C), and (B) a polyaddition compound present in a fluid or viscous form above the reaction or processing temperature and contains uretdione groups and, optionally, free isocyanate groups and based on aliphatic and/or cycloaliphatic diisocyanates, and (C) at least one active or reactively activatable Lewis acid catalyst and (D) other catalysts known from urethane chemistry and (E) auxiliary materials and additives that are known per se, where D) and E) can be added.
2. Masses according to claim 1, in which the component (A) comprises a polymer compound having hydroxyl groups such as, for example, polyacrylates, polyethers, polyesters, and oligo- and/or polyepoxides.
3. Masses according to claim 1, in which the component (B) comprises a polyaddition compound based on isophorone diisocyanate and/or hexamethylene diisocyanate having uretdione groups and optionally free isocyanate groups.
4. Masses according to claim 1, in which the reactive agent is an epoxy compound and/or an oxazoline compound.
5. Masses according to claim 1, in which the component (C) comprises at least one metalorganic catalyst of the general formula
$$R_2MeX_2$$

in which

Me means metal,

R means alkyl residue, and

X means carboxyl residue.

6. Masses according to claim 1, in which the component (C) comprises at least one metalorganic catalyst of the general formula



in which

Me means metal,

R means alkyl residue, and

Y means alcoholate residue.

7. Hardenable masses according to claim 1, characterized in that the component (C) comprises at least one metalorganic catalyst of the general formula



in which

Me means metal,

Z means acteylacetonate residue, and

n means 2 or 3.

8. Masses according to claim 1, in which the component (C) comprises at least one derivative of a metalorganic catalyst according to claims 5 to 7.

9. Masses according to claim 1, in which the component (C) comprises any unspecified mixtures of the above-mentioned metalorganic catalysts and derivatives according to claims 5 to 8.

10. Masses according to claim 1, in which the component (D) comprises nucleophillic substances.

11. Masses according to claim 1, in which the component (A) has a hydroxyl number of 25 to 200 and an average molecular weight of 1,000 to 10,000.

12. Process for the production of hardenable masses containing uretdione groups according to at least one of claims 1 to 11, in which masses that are not

cross-linked containing uretdione groups are used as original material, which consist of (A) a linear or branched bonding agent component having terminal and/or side chain hydroxyl groups with a hydroxyl number of 25 to 400 and an average molecular weight of 400 to 20,000, which is present in a fluid or viscous form above the reaction or processing temperature, with (A1) either the bonding agent component being free of carboxyl groups or (A2) the concentration of carboxyl groups being less than the concentration of the active catalyst (C) or (A3), in the case of a higher concentration of carboxyl groups in relation to the catalyst concentration (C) used, such an amount of reactive agent is added that is necessary to block the amount of carboxyl groups in order to realize a required concentration of the active catalyst (C), and (B) a polyaddition compound present in a fluid or viscous form above the reaction or processing temperature and contains uretdione groups and, optionally, free isocyanate groups and based on aliphatic and/or cycloaliphatic diisocyanates, and (C) at least one active or reactively activatable Lewis acid catalyst, and (D) other catalysts known from urethane chemistry and (E) auxiliary materials and additives that are known per se, where D) and E) can be added, these original materials are homogenized in solution and/or in melt at the longest until an increase in molar mass can be verified, then the solution or melt is quickly cooled to below the reaction temperature of the mass and subsequently the hardenable mass can be stored and then or subsequently to cooling the further processing of the hardenable mass to complete cross-linking is performed, with the temperature being linearly and/or non-linearly increased and/or kept constant at the reaction temperature sufficiently long until essentially no more reaction heat can be verified by the use of DSC measurements.

13. Process according to claim 12, in which the homogenization of the hardenable masses in the melt takes place in a laboratory kneader or in a co-kneader and/or an extruder.

14. Process according to claim 12, in which the homogenization of the

hardenable masses occurs at temperatures less than or equal to 110°C, preferably between 50 and 100°C.

15. Process according to claim 12, in which the homogenization of the hardenable mass is performed for up to 30 min.

16. Process according to claim 12, in which the cooling below the reaction temperature occurs after the homogenization of the hardenable masses by insertion of the melt into liquid nitrogen or by applying it to a cooling belt.

17. Process according to claim 12, in which at least one of the components (A) to (E), preferably (A) and (B), is used in a fluid form.

18. Process according to claim 12, in which the temperature is increased linearly and/or non-linearly in a range of preferably 20 K above the homogenization temperature up to 200°C, preferably up to 180°C.

19. Process according to claim 12, in which the addition of the catalyst or catalyst mixture (C; D) as a batch is performed after the homogenization of the components (A), (B), and (E) at reduced temperatures.

20. Process according to claim 12, in which the homogenization of the hardenable masses occurs in a melt.

21. Process according to claim 12, in which the homogenization of the hardenable masses is performed in one or more stages in a melt, with the catalyst being added at lower temperatures in the case of single-stage homogenization and, in the case of multi-stage homogenization, is not added until the second stage at lower temperatures.

22. Process according to claim 12, in which the temperature is increased in stages and the temperature is kept constant after every increasing step for a time period of 1 to 60 minutes, more advantageously 5 to 30 minutes.

23. Process according to claim 12, in which the temperature is increased in two stages, with the second increase in temperature being performed immediately after the first stage or temporally later.

24. Use of the masses according to claims 1 to 11 for coating heat-resistant and

thermolabile substrates, for masking components, as a treatable, hardenable molding compound and a thermally hardenable surfacer.

Patented by the U.S. Patent and Trademark Office



**ABSTRACT**

The invention is used in the fields of chemistry and relates to hardenable materials which can be used for producing lacquers. The aim of the invention is to provide materials which harden at low temperatures in the same amount of time as the others. This is achieved by using hardenable materials containing uretdione groups and containing (A) a binding agent constituent, whereby this component either (A1) does not contain carboxyl groups, or (A2) the concentration of carboxyl groups is less than that of the catalyst (C) or (A3) in the case of a high level of concentration, a quantity of a reactive agent is added. The hardenable materials also contain (B) a polyaddition compound which comprises uretdione groups, and (C) at least one Lewis acid catalyst. The aim of the invention is also achieved using a method for producing materials of this type in which the starting materials are homogenized in a solution and/or in a melt, the solution and/or melt is then rapidly cooled, and the subsequent processing is carried out afterwards to effect a complete cross-linking.

# Declaration and Power of Attorney For Utility or Design Patent Application

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(Number)	(Country)
(Number)	(Land)

<u>10/December/1998</u>
(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)
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Priority Claimed  
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Yes	No
Ja	Nein
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Die ernannten Patenanwlte sind zur Zeit:

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Full name of sole or first inventor  
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Unterschrift des Erfinders Datum

Inventor's signature Date

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## German Language Utility or Design Patent Application Declaration

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Unterschrift des fünften Erfinders      Datum	Fifth Inventor's Signature      Date
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Postanschrift	Post Office Address
Vor-und Nachname des sechsten Miterfinders (falls zutreffend)	Full name of sixth inventor, if any
Unterschrift des sechsten Erfinders      Datum	Sixth Inventor's signature      Date
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